

# Scanning Photoluminescence in $\text{Si}_3\text{N}_4$ Antireflected Coating of mc-Si

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## ABSTRACT

We report on spectroscopic photoluminescence (PL) mapping performed at room temperature in commercially grade mc-Si ribbon wafers for solar cells. Besides a standard band-to-band luminescence of silicon with maximum at 1.09eV, a broad visible PL band at 1.94eV is observed under UV excitation of mc-Si wafers covered with  $\text{Si}_3\text{N}_4$  layer. Scanning PL demonstrated that both bands (a) are distributed inhomogeneously in full-size wafers, and (b) their intensity profiles are not related to each other. Additionally, the visible PL band exhibits a reversible photo-quenching of the intensity under 325nm He-Cd laser excitation, which depends on the excitation intensity and can be recovered after heating the sample at 300°C for a few minutes. We demonstrate the possibility to create luminescence micro-pattern on  $\text{Si}_3\text{N}_4$  layer using UV laser beam.

**1. Introduction.** Thin amorphous silicon nitride ( $\text{Si}_3\text{N}_4$ ) PECVD films are routinely used in multi-crystalline silicon (mc-Si) solar cell production. A principal function of the films is to provide anti-reflecting coating to enhance solar light penetration into silicon. On the other hand, it is recognized that  $\text{Si}_3\text{N}_4$  deposition followed by a low-temperature annealing stimulates hydrogen incorporation, which benefits the electronic quality of silicon by increasing the minority carrier lifetime [1]. There is a current need for diagnostics and control of the  $\text{Si}_3\text{N}_4$  film quality to achieve high-efficient mc-Si solar cells. We report here on room temperature scanning photoluminescence (PL) study performed on  $\text{Si}_3\text{N}_4$  coated mc-Si ribbon wafers.

**2. Samples and experimental.** Two sets of commercial-grade (i) as-grown ribbon wafers and (ii) similar wafers covered with  $\text{Si}_3\text{N}_4$  layer with 150mm x 80mm size and 300  $\mu\text{m}$  thickness were available for the PL study (Evergreen Solar). The details of scanning PL set-up were described elsewhere [2]. A primary modification of the PL system employed in this study was the usage of the ultra-violet CW He-Cd laser (325nm, 55mW) as the PL excitation source. One of two photo-detectors was used: photomultiplier tube at 400nm to 800nm spectral range and liquid nitrogen cooled Ge-diode at 800nm to 1,700nm. Selection of the detector allowed optimization of the sensitivity of the PL system. The PL spectra were corrected to the spectral response of the optical system.

## 3. Results

### (a) PL spectroscopy and mapping

Strong “yellow” luminescence with the maximum at 1.94eV is observed at room temperature on  $\text{Si}_3\text{N}_4$  coated wafers excited by He-Cd laser as shown in Figure 1. No visible PL is found in as-grown wafers without  $\text{Si}_3\text{N}_4$  layer. This proves that visible PL originates from the  $\text{Si}_3\text{N}_4$  layer itself. A small shoulder at  $\sim 1.1\text{eV}$  is due to luminescence of mc-Si and attributed to band-to-band recombination in silicon. For comparison, we show in Figure 1 the spectrum of the band-to-band luminescence measured on the same wafer using AlGaAs laser diode excitation ( $\lambda_{\text{ex}} = 800\text{nm}$ ). The spectral shape and maximum position of the visible PL are similar to the luminescence attributed to the radiative electron-hole recombination at the band tail states in  $\text{Si}_3\text{N}_4$  [3].

We employed room temperature PL mapping technique to analyze the distributions of the band-to-band ( $I_{\text{bb}}$ ) and visible ( $I_{\text{SiN}}$ ) PL intensity across the wafer. The PL map of visible PL from  $\text{Si}_3\text{N}_4$  was found to be inhomogeneous as shown in Fig.2a

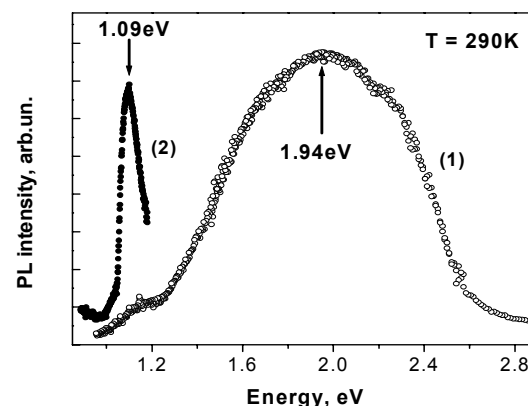


Figure 1. Room temperature PL spectra on the mc-Si wafer with  $\text{Si}_3\text{N}_4$  anti-reflecting coating at two different excitations: (1) – He-Cd laser (325nm), (2) AlGaAs laser diode (800nm). Spectral maxima of the band-to-band and band-tail PL are shown by arrows.

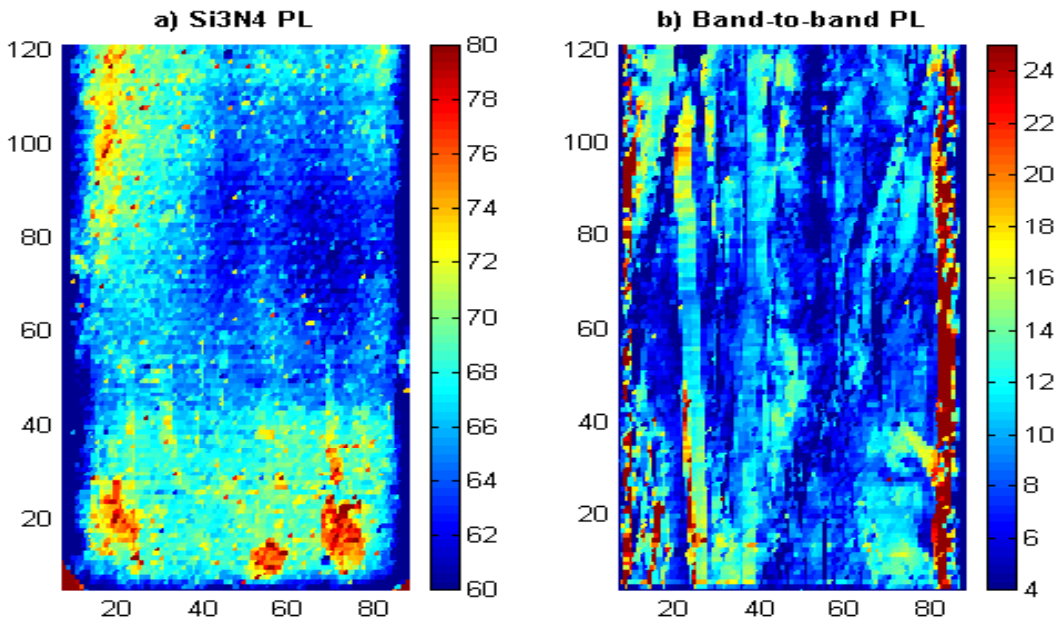


Figure 2. Room temperature PL mapping of (a) the visible luminescence from Si<sub>3</sub>N<sub>4</sub> layer under 325nm He-Cd laser excitation (1.94eV), and (b) band-to-band luminescence of mc-Si under 800nm laser excitation (1.09eV). The mapped area is 85mm x 120mm with 1mm step.

The half-width of the PL histogram revealed 18% of the intensity variation. Figure 2b shows band-to-band PL map measured at approximately the same area on the wafer using 800nm diode laser excitation. Comparing  $I_{bb}$  and  $I_{SiN}$  maps in Figure 2, it is obvious that the topographies of both maps are not related. This is not surprising, considering the fact that the  $I_{bb}$  map reflects distribution of the minority carrier lifetime [2]. Specifically, there is no clear correlation between visible PL intensity and high/low lifetime areas in mc-Si. At the same time, more correlative study has to be done to establish a potential role of  $I_{SiC}$  profile on the lifetime upgrade in mc-Si wafers.

**(b) PL quenching and patterning**

We found that  $I_{SiN}$  intensity is gradually reduced under prolonged sample illumination with He-Cd laser. The kinetics of the PL quenching is measured at different excitation power density and presented in Figure 3. Entire visible emission is a subject of photo-quenching, i.e. no spectral dependence in quenching rate is observed. At different excitation power density, the kinetics can be satisfactorily fit by a “stretched exponential” function, which is commonly observed in disordered systems and intensively studied in hydrogenated  $\alpha$ -Si films [4],

$$I(t) = I_0 \exp(-[t/\tau]^\beta) + \text{const}, \tag{1}$$

where  $\tau$  is the quenching time,  $\beta$  is a stretch parameter.

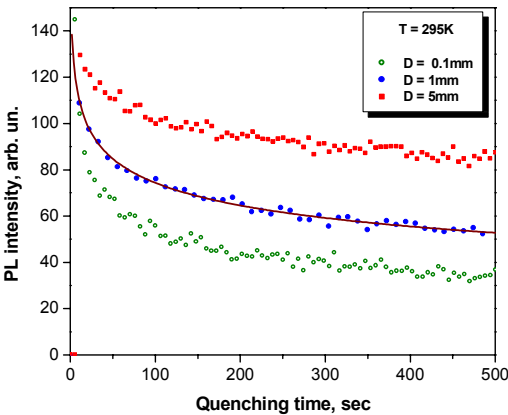


Figure 3. The kinetics of photo-quenching observed on “visible” luminescence of Si<sub>3</sub>N<sub>4</sub> films. Three curves correspond to variation of the He-Cd laser power density using different laser spot. Solid line shows a fit of one of PL kinetics by stretched exponent equation (1).

In Table 1 we summarized calculated values of quenching time ( $\tau$ ) and stretch parameter ( $\beta$ ) at different excitations. We observe a strong dependence of the quenching time on the excitation power density, and negligible variation of the stretch parameter.

Table 1

Excitation power density, W/cm <sup>2</sup>	$\tau$ , min	$\beta$
~130 (focused beam)	16	0.339
2.5	87	0.381
1.5	112	0.357
1.1	114	0.397
0.5	133	0.375

We found that photo-quenching kinetics is very similar both in the areas with high and low initial visible luminescence. At room temperature we have not seen a noticeable PL recovery within 24 hours of monitoring. An important observation is that the recovery of the initial PL intensity is found at higher temperatures and shows a thermally activated behavior, i.e. the higher the temperature, the faster the recovery rate. Specifically, we have found 80% recovery of the PL intensity at 300°C after 30 minutes of annealing. Keeping this in mind, the observed PL photo-quenching reveals a metastable process in Si<sub>3</sub>N<sub>4</sub> film under UV excitation.

The absence of fast recovery processes at room temperature allows creating a luminescence pattern on Si<sub>3</sub>N<sub>4</sub> layer. Figure 4 illustrates this. The pattern was produced by moving stage with the wafer with respect to the unfocused laser beam in a programmed mode. Quenching time in this case is 3 minutes per point. After the quenching was finished, entire wafer was subject to a new PL mapping, showing the image in Figure 4.

**4. Conclusions.** We applied scanning room-temperature photoluminescence to access inhomogeneity of recombination properties in amorphous Si<sub>3</sub>N<sub>4</sub> PECVD layers deposited on mc-Si wafer. Strong visible PL band with the maximum at 1.94eV is observed under the UV excitation. The distribution of visible PL intensity across the wafer is different compared to band-to-band PL of the Si substrate. The PL from silicon nitride layer exhibits reversible photo-degradation during prolonged exposure by the UV illumination. PL recovery after illumination is observed only at high temperatures. We suggest that PL mapping reveal a distribution of the atomic hydrogen in the Si<sub>3</sub>N<sub>4</sub> films, which is critical technological element to defect passivation in crystalline Si. The reason for inhomogeneity is tentatively related to hydrogen passivation of the non-

radiative defects in the film. Additional experiments to confirm this mechanism are currently in progress.

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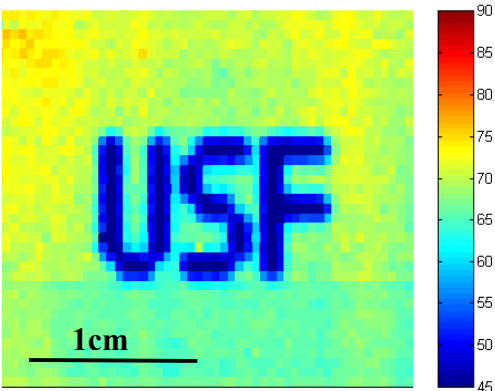


Figure 4. Luminescence pattern produced on Si<sub>3</sub>N<sub>4</sub> layer by unfocused HeCd laser beam. The diameter of the laser beam is 1.5mm. The burning time is 3 min per point. Luminescence mapping size is 25mm x 20mm, step = 0.5mm.